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DETECTION OF NO_x, C_2H_4 CONCENTRATIONS BY USING CO AND CO_2 LASERS

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A laser, especially the infrared line-tunable laser, opens up a new way to monitor the atmospheric environment, and already has gotten effective practical application. One of the most serious problems in open-path remote measurement at atmospheric pressure is the broadening effect which leads to increased linewidths, spectral interferences, and, as a result, tends to reduce detection sensitivity, so measuring laser wavelengths should be selected carefully, and interaction between the measuring wavelength and gas to be measured must be known very well. Therefore, N_2O, NO, NO_2, CH_4, NH_3 and C_2H_4 absorption properties at some lines of CO and CO_2 line-tunable lasers were studied in our laboratory. The absorption coefficients of NO, NO_2 and C_2H_4; some results on detection of NO_x, C_2H_4 concentrations in both laboratory and field; and selection of measuring wavelengths and error analysis are discussed in this paper.

1. EXPERIMENT

Fig.1 is a schematic diagram of the experimental system used for absorption coefficient measurements and simulation detection of NO_x, C_2H_4 concentrations. The whole experimental equipment consists of a laser source, external optical system, sample absorption cell, detector, lock-in amplifier, and recording and data processing systems. CO and CO_2 line-tunable lases are

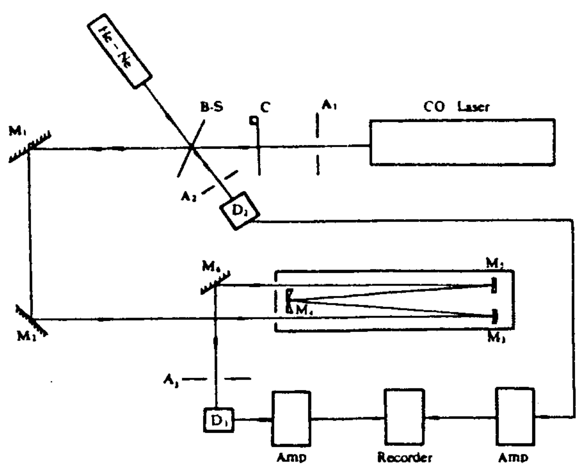

Fig.1 Schematic diagram of the experimental system

used as a radiation source; the typical output power of single laser line is about 1 watt. The sample cell is a multi-path absorption cell with a physical length of 3m. The infrared spectrophotometer is used as a line-monitoring device. Absorption coefficients at a given laser line are obtained from a transmittance, which is measured by using the ratio of the measuring and controlling beams in order to eliminate errors caused by instability of the laser source and possible variation of instrumental constant.

2. NO, NO_2, C_2H_4 ABSORPTION COEFFICIENTS

A vibration-rotational spectrum of NO 5.3 μ absorption band consists of two subbands, as a result, a double-line series of NO spectrum is produced. Line intensities of subband $^2\Pi_{1/2}$ are about two times more than that of subband $^2\Pi_{3/2}$. A wavenumber range of NO 5.3 μ absorption band is about $1985 cm^{-1} - 1777 cm^{-1}$. The two subbands can be easily separated by using a laser as a monochromatic radiation source according to absorption properties of NO 5.3 μ band. As wavelength range of used CO laser is limited, the P-branch of NO 5.3 μ absorption band was studied only. The selected laser frequencies and obtained NO absorption coefficients are listed in Tab.1.

Tab.1 Absorption coefficients of NO

$\nu_{CO}(cm^{-1})$	$k_{NO}(atm\text{-}cm)^{-1}$	$k_{H_2O}(cm^2/g)$	$u_{NO}(atm\text{-}cm/km)$
1784.153	0.41	40.26	34.37
1788.397	0.32	54.54	59.66
1801.120	0.34	71.63	72.88
1826.217	0.34	51.80	53.01
1829.592	1.21	362.40	104.70
1834.593	0.27	14.77	19.08
1838.708	0.24	12.49	18.52
1842.808	3.29	40.49	4.31
1847.131	0.33	27.20	28.67
1859.842	0.37	19.31	18.42
1863.655	1.07	8.71	2.86
1876.630	0.12	20.20	57.48
1880.901	0.63	2.29	1.28

NO_2 6.2 μ absorption band is an A-type band; its spectral range is about $1660 - 1550 cm^{-1}$; the high resolution spectrum of this band shows a very complicated spectral structure, that is, lines of this band seriously overlap and mix. Absorption coefficients of NO_2 at 29 CO laser frequencies are given in Tab.2. Absorption coefficients of water vapor at all listed laser frequencies are also given in Tab.1 and Tab.2 in order to provide reliable information for suitable wavelength selection and reasonable data processing in detection of NO

Tab.2 Absorption coefficients of NO_2

ν_{CO} (cm^{-1})	k_{NO_2} (atm-cm)$^{-1}$	k_{H_2O} (cm^2/g)	u_{NO_2} (atm-cm /km)	ν_{CO} (cm^{-1})	k_{NO_2} (atm-cm)$^{-1}$	k_{H_2O} (cm^2/g)	u_{NO_2} (atm-cm /km)
1575.200	8.3	76.57	3.22	1614.909	23.38	110.5	1.65
1580.778	10.1	62.63	2.17	1618.699	21.44	101.7	1.66
1582.880	15.5	33.09	0.75	1619.564	32.35	66.29	0.72
1584.359	8.6	25.57	1.04	1622.455	76.91	417.2	1.90
1587.907	45.6	18.69	0.14	1626.175	83.64	64.06	0.27
1590.457	32.4	35.77	0.39	1629.862	71.86	36.97	0.18
1595.609	53.6	106.8	0.70	1631.721	76.83	47.63	0.22
1597.929	28.7	34.06	0.41	1633.313	74.76	76.11	0.36
1599.488	41.2	18.83	0.16	1640.743	12.87	66.60	1.81
1601.614	19.2	19.00	0.35	1643.272	7.28	55.94	2.69
1603.386	55.4	33.89	0.21	1644.277	10.24	70.29	2.40
1605.265	41.4	22.03	0.19	1647.067	9.51	468.2	17.24
1607.252	54.9	22.23	0.14	1650.819	4.48	200.1	15.62
1611.084	50.4	62.31	0.43	1656.260	1.63	129.4	27.76
1612.487	50.7	33.86	0.23				

and NO_2 concentrations. The u_{NO} in column 4 of Tab.1 and u_{NO_2} in column 4, 8 of Tab.2 denote equivalent contents of NO and NO_2, respectively; these values correspond to such atmospheric transmittance to which corresponds the water vapor content of 0.35g/km in the atmosphere.

Absorption of ethylene at CO_2 laser lines is essentially due to the intense ν_7 C-type infrared band which presents a strong Q-branch near 950 cm-1; its R and P branches cover the region from 1100 to 800 cm^{-1}. So it is not difficult to find some coincidences between C_2H_4 absorption lines and CO_2 laser lines. As an example, the absorption coefficients of ethylene at P-branch of CO_2 00^01-10^00 band are listed in Tab.3.

Tab.3 C_2H_4 Absorption coefficients k(atm-cm)$^{-1}$at 285K

laser line	k	MSE	laser line	k	MSE
10p6	2.25	0.10	10p24	2.47	0.10
10p8	1.85	0.09	10p26	1.97	0.17
10p10	3.54	0.37	10p28	1.36	0.05
10p12	4.92	0.58	10p30	1.56	0.05
10p14	33.47	2.04	10p32	1.18	0.07
10p16	5.09	0.53	10p34	1.63	0.05
10p18	3.40	0.22	10p36	1.34	0.05
10p20	1.98	0.14	10p38	2.12	0.10
10p22	1.57	0.09			

3. DETECTION OF NO_x, C_2H_4 CONCENTRATIONS

Based on the above obtained absorption coefficients, a simulation detection of NO, NO_2 and C_2H_4 concentrations by means of the two-wavelength differential absorption method was made in our laboratory. Several sets of laser lines and given concentrations of samples were used for this purpose. The diagram of used equipment is similar to Fig.1. Results for all measurements are more satisfied, the variation range of relative error in concentration detection for NO is 2-15%, and for NO_2, C_2H_4 is less than 10%.

Moreover, a detection of NO concentration in the actual urban atmosphere was made by using CO laser lines of 1863.655 and 1842.808 cm^{-1} as the measuring wavelengths, and of 1880.901 cm^{-1} as a reference wavelength. The results show that NO concentration produced by traveling automobiles may go up to about 1 atm-cm/km, that is about 10-20 times higher than the NO background concentration.

4. ERROR ANALYSIS

Errors in long-path laser monitoring NO, NO_2, C_2H_4 concentrations are mainly caused by factors such as accuracy in absorption coefficient measurement, selection of used laser lines, interference of nonmonitored gases in the atmosphere and atmospheric aerosol, and atmospheric turbulence as well.

It should be noted firstly that accuracy of NO, NO_2 and C_2H_4 absorption coefficients at corresponding CO, CO_2 laser lines is not satisfied enough up to now, although many works have been done in this respect. For example, a typical discrepancy in C_2H_4 absorption coefficients at CO_2 laser lines measured by various authors varies from 10% to 40%, as a result, a corresponding error in ethylene concentration detection is produced by this reason. Another problem to be emphasized is an interference of nonmonitored atmospheric species. Here, the most important gases are carbon dioxide and water vapour, whose absorptions cover almost the whole infrared region and strongly vary with a selected wavelength. For example, the smallest value of water vapour absorption coefficient at all CO laser lines within the 6.2 μ NO_2 band is about 20 cm^2/g, in other words, the equivalent content of NO_2 caused by absorption effect of water vapour in the middle-latitude winter atmosphere is about 0.2 atm-cm/km.